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Born-Oppenheimer potential and the polarisable model of lattice dynamics

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The two well known polarisable models in lattice dynamics are the shell model (SM), (Woods *et al* 1960) and the deformation dipole model (DDM)(Hardy 1959, 1962). Cowley *et al* (1963) and Basu (1974) discussed in detail the relation between these models. But these discussions are based on the dynamical matrices and not on the energy expression corresponding to each model. There are certain obvious advantages if one can write down the energy expressions for these models

To write the Born-Oppenheimer effective potential energy function in terms of ionic distances alone is almost impossible for any of these models It is, however, simple to write the energy in terms of ionic dipole moments and ionic distances.

In DDM, the dipole moment of each ion is separated in two parts, electrical and deformation and is written for the ith ion as,

$$\boldsymbol{\mu}_i = \boldsymbol{\mu}_i^e + \boldsymbol{\mu}_i^d,$$

where
$$\boldsymbol{\mu}_i = \alpha_i \boldsymbol{E}_i \; ; \; \boldsymbol{\mu}_i^d = -\sum_j{}' \, m_i(R_{ij}) \, \frac{\boldsymbol{R}_{ij}}{R_{ij}} \sum_j D(ji) \boldsymbol{U}_j \qquad \ldots \quad (1)$$

The electrical part is determined by the polarisability α_i and the net electrical field at the position of the ith ion The deformation part is assumed to be given by the short range parameter m_i or the deformation dipole matrix D, which can be related to the Szigeti charge defect (Born & Huang 1954) In the above $\boldsymbol{R}_i = \boldsymbol{R}_{0i} + \boldsymbol{U}_i$, $\boldsymbol{R}_{ij} = \boldsymbol{R}_i - \boldsymbol{R}_j$ and $\boldsymbol{U}_i$ are the displacement from the equilibrium position $\boldsymbol{R}_{oi}$. Including a short range repulsive interaction ϕ_{ij} the total energy of the crystal according to DDM may be written as,

$$W = \tfrac{1}{2} \sum_{ij}{}' \frac{Z_i Z_j}{R_{ij}} - \sum_i \boldsymbol{\mu}_i \boldsymbol{E}_i^m - \tfrac{1}{2} \sum_i \boldsymbol{\mu}_i . \boldsymbol{E}_i^\mu + \tfrac{1}{2} \Sigma (\boldsymbol{\mu}_i^e)^2 / \alpha_1 + \tfrac{1}{2} \sum_{i,j}{}' \phi_{ij}. \qquad (2)$$

Here the first three terms give the electrical interaction between the monopoles Z_i and dipoles $\boldsymbol{\mu}_i$ at each ion site, $\boldsymbol{E}_i^m$ is the electrical field at the ith ion due to monopole charges at other sites and $\boldsymbol{E}_i^\mu$ is the corresponding dipole field. The fourth term gives the self energy of the electrical part of the dipoles. It can be shown that the energy expression (2) leads to the same dynamical matrix as obtained by Hardy (1959, 1962) for DDM.

The monopole field $\boldsymbol{E}_i^m$ and the field $\boldsymbol{E}_i^\mu(d)$ by deformation dipoles can be easily expressed in terms of the ionic coordinates,

$$\boldsymbol{E}_i^m = \sum_j{}' Z_j \frac{\boldsymbol{R}_{ij}}{R_{ij}^3}\,;\ \boldsymbol{E}_i^\mu(d) = \sum_{j,k} \tau_{ij} m_j(R_{jk}) \frac{\boldsymbol{R}_{jk}}{R_{jk}}$$

$$\tau_{ij} = \frac{3\boldsymbol{R}_{ij}\boldsymbol{R}_{ij}}{R_{ij}^5} - \frac{\delta_{ij}}{R_{ij}^3}\,. \qquad \ldots\ (3)$$

It is, however, more difficult to express the field due to electrical dipoles $\boldsymbol{E}_i^\mu(e)$ in terms of $\boldsymbol{R}_{ij}$. One may write,

$$\boldsymbol{E}_i^\mu(e) = \sum_{jk} (1-\tau\alpha)_{ij}^{-1}(\tau\alpha)_{jk}(\boldsymbol{E}_k^m + \boldsymbol{E}_k^\mu(d))$$

where,
$$(\tau\alpha)_{ij} = \tau_{ij}\alpha_j \qquad \ldots\ (4)$$

Eq (4) is not very useful because of the inverse matrix If, however, we consider only the first order effect of polarisability then we may write,

$$\boldsymbol{E}_i^\mu(e) = \sum_j{}' \tau_{ij}\alpha_j \boldsymbol{E}_j^m \qquad \ldots\ (5)$$

In this linear approximation, the *B-O* potential energy for DDM can be written in the simple form,

$$W = \frac{1}{2}\sum_{ij}{}' \phi_{ij} + \frac{1}{2}\sum_{ij}{}' \frac{Z_i Z_j}{R_{ij}} - \frac{1}{2}\sum_{ijk}{}' \alpha_i Z_j Z_k \frac{\boldsymbol{R}_{ij}.\boldsymbol{R}_{ik}}{R_{ij}^3 R_{ik}^3} + \sum_{ijk}{}' Z_k m_i(R_{ij}) \frac{\boldsymbol{R}_{ij}.\boldsymbol{R}_{ik}}{R_{ij}R_{ik}^3}\,. \qquad \ldots\ (6)$$

The last two terms in eq (6) represent the effective interaction due to electrical and short range polarisability of the ions It is interesting to notice that in the linear approximation polarisation implies effective three body interaction only and no higher many body interaction exists In the usual 6×6 matrix notation (Basu *et al* 1974) the dynamical matrix corresponding to the energy expression (6) may be written as,

$$M = R + ZCZ - ZC\alpha CZ + ZCD^r + D'CZ \qquad \ldots\ (7)$$

To test how far the linear expression is good we have calculated the dispersion relation for NaI crystal along (100) and (111) directions using the same parameters as given by Karo & Hardy (1963) in their complete DDM calculations The results are shown in table 1 It is found that the linear approximation is quite good for transverse branches and reproduces the exact DDM values But, as expected, for longitudinal branches the effect of polarisability is large and the linear approximation gives poor agreement However, in eq. (5) we may retain terms quadratic in α. Values of frequency calculated according to this quadratic approximation are given in table 1 for the longitudinal branches. The agreement improves somewhat but for some points the discrepancy is as large as twenty per cent.

Table 1. Comparison between DDM (exact) and DDM(linear approximation) calculation for transverse branches and DDM (exact) and DDM (quadratic approximation) calculation for longitudinal branches of normal mode frequencies ω of NaI for wave vector q along (100) and (111) direction For each q/q_{max} the upper figure corresponds to (100) direction and the lower figure to (111) direction. Rigid ion (RI) values are also given ω in units of 10^{13} read sec^{-1}

q/q_{max}	TA			TO			LA			LO		
	RI	DDM (linear)	DDM (exact)	RI	DDM (linear)	DDM (exact)	RI	DDM (quadratic)	DDM (exact)	RI	DDM (quadratic)	DDM (exact)
0	0	0	0	2 01	2.20	2 20	0	,	0	4 17	3 96	3 20
0 2	0.27	0 27	0 27	2 05	2 24	2 22	0 52	0 54	0 54	4 09	3 79	3 14
	0 27	0 27	0 27	2.01	2.18	2 18	0.43	0 42	0 41	4 13	3 92	3 33
0 4	0 51	0 49	0.48	2 12	2 31	2 27	0 95	0.99	0 98	3 87	3 37	2 83
	0 50	0.51	0 51	2 00	2 14	2.13	0 84	0.82	0 79	4 03	3 82	3 40
0 6	0.69	0 63	0 60	2 23	2 42	2.35	1 25	1.32	1 60	3 61	3 21	2 57
	0 69	0.77	0.73	2.00	2 07	2 06	1 20	1.16	1.05	3 89	3 73	3 51
0 8	0 80	0 69	0 67	2 31	2 46	2 38	1 37	1.32	1 11	3 41	2 91	2 64
	0 81	0.87	0 86	1 99	2.00	2.00	1 47	1 37	1 25	3 75	3 68	3 60
1 0	0 83	0 73	0.70	2 35	2 48	2.41	1 38	1.26	1.05	3 34	3.24	2 73
	0 85	0.93	0.92	1.99	1.98	1.95	1.57	1 41	1 29	3 70	3 68	3.68

In shell model, every ion is divided into a core of charge $Z_i + Y_i$ and a shell of charge $-Y_i$ If $\boldsymbol{R}_i$ and $\boldsymbol{R}_i^s$ represent the position of the core and the shell respectively then the dipole moment and the self energy of each ion is given by,

$$\boldsymbol{\mu}_i = -Y_i(\boldsymbol{R}_i^s - \boldsymbol{R}_i)$$

$$\text{self- energy} = \tfrac{1}{2}K_i(R_i^s - R_i)^2 = \mu_i^2/2\alpha_i \qquad \ldots (8)$$

where, $\alpha_i = Y_i^2/K_i$ and K_i is the core-shell spring constant Assuming the overlap interaction to act through shells only, we may write the energy expression for SM,

$$W = \frac{1}{2}\Sigma'_{i,j}\frac{Z_iZ_j}{R_{ij}} - \Sigma_i \boldsymbol{\mu}_i.\boldsymbol{E}_i^m - \frac{1}{2}\Sigma_i \boldsymbol{\mu}_i \boldsymbol{E}_i^\mu + \frac{1}{2}\Sigma_i\frac{\mu_i^2}{\alpha_i} + \frac{1}{2}\Sigma'_{ij}\phi\left(\left|\boldsymbol{R}_{ij} - \frac{\boldsymbol{\mu}_i}{Y_i} + \frac{\boldsymbol{\mu}_j}{Y_j}\right.\right) \qquad (9)$$

where, the dipole moment $\boldsymbol{\mu}_i$ is determined by the ionic coordinates through the adiabatic equation,

$$\frac{\partial W}{\partial \boldsymbol{\mu}_i} = -\boldsymbol{E}_i^m - \boldsymbol{E}_i^\mu + \frac{\boldsymbol{\mu}_i}{\alpha_i} - \frac{1}{Y_i}\Sigma_j\left((\phi'(R)\frac{R}{R}\right)\boldsymbol{R} = \boldsymbol{R}_{ij} - \boldsymbol{\mu}_i|Y_i + \boldsymbol{\mu}_j|Y_j = 0. \quad \ldots (10)$$

By expanding $\boldsymbol{R}_l$ about the equilibrium configuration one can prove that eqs (9) and (10) lead to the shell model equations for lattice dynamics. Comparing eq. (9) with eq. (2) we notice that the essential difference is in the self energy term and the overlap term. The self energy term in SM includes the total dipole moment of an ion. Moreover, in SM the overlap term gets modified which is not considered in DDM. If we expand the overlap energy in terms of $\boldsymbol{\mu}$ then upto terms linear in $\boldsymbol{\mu}$ we may write,

$$\text{overlap interaction between } i-j \text{ ion} \simeq \phi(R_{ij})+\phi(R_{ij})\left(\frac{\boldsymbol{\mu}_i}{\mu_{0i}}\frac{\boldsymbol{R}_{ij}}{R_{ij}}+\frac{\boldsymbol{\mu}_j}{\mu_{0j}}\frac{\boldsymbol{R}_{ji}}{R_{ij}}\right) \quad (11)$$

where, $\mu_{0i} = Y_i\rho$, ρ being the hardness parameter of the overlap interaction. The second term in eq. (11) represents the change in the overlap interaction due to the ions having dipole moments. μ_{01} and μ_{02} may be regarded as two characteristic constants associated with the polarisability of the two types of ions. Looked at in this way we can describe the shell model in terms of the meaningful parameters α_1, α_2, μ_{01} and μ_{02} rather than the unphysical parameters, spring constants charges.

As in the case of DDM, to get the $B-O$ energy corresponding to SM we confine and shell to the first order effect of polarisability. Then from eq (10) we may write,

$$\boldsymbol{\mu}_i = \alpha_i \boldsymbol{E}_i^m - \frac{\alpha_i}{\mu_{0i}} \sum_j \phi(R_{ij}) \frac{\boldsymbol{R}_{ij}}{R_{ij}} \quad \ldots \quad (12)$$

Here we have neglected a small correction to α_i due to overlap interaction. It is interesting to notice that in the linear approximation, shell model leads to a split up of the total dipole moment into an electrical part and a deformation part as in DDM. Comparing the two expressions we find that

$$m_i(R_{ij}) = \frac{\alpha_i}{\mu_i}\ \phi(R_{ij}) \quad (13)$$

In the linear approximation, we can write down the shell model energy in eq. (9) in terms of ionic coordinates alone and the result is,

$$W(SM) = W(DDM) - \frac{1}{2} \sum_{ijk}{}' \frac{m_i(R_{ij})m_i(R_{ik})}{\alpha_i} \frac{\boldsymbol{R}_{ij}\cdot\boldsymbol{R}_{ik}}{R_{ij}R_{ik}} \quad (14)$$

where $W(DDM)$ is given by eq (6). It is noticed that in the linear approximation both the models become almost identical. The only difference is in the last term of eq (14). The contribution of this term, however, to the dynamical matrix and to the phonon frequencies is quite small.

Comparing the energy expression given by eqs. (2) and (9) for DDM and SM respectively we conclude that on the whole eq. (9) has better a priori justification The self energy expression here is in accord with the microscopic theory and the modification of the overlap interaction due to polarisation of the ions is also expected The only shortcoming of the shell model energy expression seems to be that a microscopic justification for the particular form of the overlap interaction is not easy to find and that the model neglects the quadrupole effects

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